



(19) Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) Publication number: 0 310 734 B1

(12)

EUROPEAN PATENT SPECIFICATION

(45) Date of publication of patent specification: 23.11.94 (51) Int. Cl.⁵: C08F 4/60, C08F 10/00

(21) Application number: 87870133.3

(22) Date of filing: 21.09.87

(54) Catalyst systems for producing polyolefins having a broad molecular weight distribution.

(30) Priority: 11.09.87 US 95755

(43) Date of publication of application:
12.04.89 Bulletin 89/15

(45) Publication of the grant of the patent:
23.11.94 Bulletin 94/47

(84) Designated Contracting States:
AT BE CH DE ES FR GB IT LI NL SE

(56) References cited:
EP-A- 0 128 045 EP-A- 0 128 046
EP-A- 0 129 368 EP-A- 0 185 918
EP-A- 0 197 319 US-A- 4 522 982

DIE ANGEWANDTE MAKROMOLEKULARE CHEMIE, vol. 145/146, 1986, pages 149-160, Hüthig & Wepf Verlag, Basel, CH; W. KAMINSKY: "Stereoselektive Polymerisation von Olefinen mit homogenen, chiralen Ziegler-Natta-Katalysatoren"

DIE MAKROMOLEKULARE CHEMIE/MACROMOLECULAR SYMPOSIA, vol. 3, June 1986, pages 377-387, Basel, CH; W. KAMINSKY et al.: "Olefincopolymerization with highly active soluble zirconium compounds using aluminoxane as co-catalyst"

J. AM. CHEM. SOC., vol. 106, 1984, pages 6355-6364, American Chemical Society; J.A. EWEN: "Mechanisms of stereochemical control in propylene polymerizations with soluble group 4B metallocene/methylalumoxane catalysts"

(73) Proprietor: FINA TECHNOLOGY, INC.
8350 North Central Expressway
Dallas, Texas 75206 (US)

(72) Inventor: Ewen, A. John
16615 Kentwood Avenue
Houston, Texas 77058 (US)

(74) Representative: Detroit, Jean-Claude
c/o Fina Research S.A.
Patent Department
Zone Industrielle C
B-7181 Feluy (BE)

EP 0 310 734 B1

Note: Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Description**TECHNICAL FIELD**

5 The invention relates to catalyst systems for the polymerization of olefins that produce a polymer product having a broad molecular weight distribution. These catalyst systems include at least two different chiral, stereo-rigid metallocene catalysts and an aluminum compound.

BACKGROUND

10 The present invention provides catalyst systems for use in the polymerization of olefins, especially propylene and copolymers of propylene, that produce a polymer with a broad or multimodal molecular weight distribution. These catalyst systems include a mixture of at least two different chiral, stereo-rigid metallocene catalysts.

15 The use of metallocene catalysts in the polymerization of olefins is known in the art. German Patent Application 2,608,863 discloses a catalyst system for the polymerization of ethylene which system consists of a bis(cyclopentadienyl) titanium dialkyl, an aluminum trialkyl and water. Similarly, German Patent Application 2,608,933 discloses a zirconium metallocene of the formula $(\text{cyclopentadienyl})_n\text{ZrY}_{4-n}$, wherein Y represents R, CH_2AlR_2 , $\text{CH}_2\text{CH}_2\text{AlR}_2$, or $\text{CH}_2\text{CH}(\text{AlR}_2)_2$ and where R is an alkyl or metalloclo alkyl and n is an integer within the range 1-4. This catalyst is described as being useful in the polymerization of ethylene.

20 Metallocene catalysts are known to be useful in the copolymerization of ethylene and other alphaolefins. U.S. Patent No. 4,542,199 to Kaminsky, et al. discloses a catalyst system that comprises a catalyst of the formula $(\text{cyclopentadienyl})_2\text{MeRHal}$, in which R is a halogen, a cyclopentadienyl group, or a C₁-C₆ alkyl radical; Me is a transition metal, in particular zirconium, and Hal is a halogen, in particular chlorine. The catalyst system also includes an alumoxane of the formula $\text{Al}_2\text{OR}_4(\text{Al}(\text{R})\text{-O})_n$ for a linear molecule and/or $(\text{Al}(\text{R})\text{-O})_{n+2}$ for a cyclical molecule in which n is a number from 4-20 and R is a methyl or ethyl radical. A similar catalyst system is disclosed in U.S. Patent No. 4,404,344.

25 Metallocene catalysts particularly useful in the polymerization of propylene and higher alpha-olefins are disclosed in European Patent publication No. 0185918. This Publication discloses a zirconium metallocene catalyst that includes a bridge between two cyclopentadienyl rings. The bridge is described as being a linear hydrocarbon with 1-4 carbon atoms or a cyclical hydrocarbon with 3-6 carbon atoms.

30 Other metallocene catalysts are also disclosed in european patent applications EP-A-0284707 and EP-A-0284708 both of which are inventions by the present inventor and are assigned to the same assignee. EP-A-0284708 describes a method for varying the melting points and molecular weights of polyolefins by varying the bridge and other substituents on a metallocene catalyst. EP-A-0284707 discloses a catalyst system comprising a stereo-rigid hafnium metallocene catalyst in combination with an aluminum compound. The catalyst is described by the formula $\text{R}''(\text{C}_5\text{R}'_m)_2\text{-HfQ}_p$, wherein R'' includes a bridge between the two (C₅R'm) rings. These hafnium metallocene catalysts are more stereo-specific and produce polymers with higher molecular weights than previously obtainable with metallocene catalysts.

35 The metallocene catalyst systems described above typically produce a polymer product with a relatively narrow molecular weight distribution (MWD). This distribution, as defined by Mw/Mn, is usually within the range of 2-4. For some polymer applications, it is desirable to have a narrow MWD; for others, a broad MWD is desirable.

40 U.S. Patent No. 4,530,914 discloses a catalyst system for the polymerization of ethylene to polyethylene having a broad MWD which may be bimodal or multimodal. The catalyst system comprises at least two different metallocenes that have different rate constants for the propagation and termination of ethylene polymerizations. The disclosure is limited to the production of polyethylene, and the disclosed catalyst system does not address the stereochemical problems of making useful polypropylene and other higher alpha-olefins.

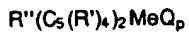
45 The present invention provides a catalyst system that may be used to polymerize almost all olefins, and not just ethylene, and to produce a polymer product with a broad MWD. The MWD may be tailored to a desired level by varying the substituents of the catalyst system.

SUMMARY OF THE INVENTION

50 The present invention provides catalyst systems for the polymerization of olefins that produce polymers with a broad or multimodal molecular weight distribution. The invention further provides a process for polymerizing olefins in the presence of the catalyst system such that the polymer product has a broad

molecular weight distribution. The invention is useful in the polymerization of all olefins, but is particularly useful in the polymerization of propylene and copolymers of propylene and other olefins.

The catalyst system of the present invention comprises at least two different metallocene catalysts which are chiral and stereo-rigid in combination with an aluminum compound. The metallocene catalysts 5 can be described by the formula:



wherein $(C_5(R')_4)$ is a cyclopentadienyl or substituted cyclopentadienyl ring; each R' may be the same or 10 each may be different, and R' is a hydrogen or a hydrocarbyl radical having 1-20 carbon atoms; R'' is an organic or inorganic group that acts as a bridge between the two $(C_5(R')_4)$ rings and serves to make the catalyst stereo-rigid; Me is a Group 4b, 5b, or 6b metal of the Periodic Table; Q is a hydrocarbon radical having 1-20 carbon atoms or is a halogen; and $O \leq 3$. The catalysts may differ by having different metals 15 as the Me group or by having different groups for any of the ligands or substituent groups. By varying the catalyst combinations, it is possible to make polymer products with varying molecular weight distributions.

The catalyst system also includes an aluminum compound which is preferably an alumoxane. The alumoxane can be either linear, cyclic, or a combination of linear and cyclic. In another embodiment of the invention, the aluminum compound may include a mixture of alumoxane and trimethyl aluminum. In addition, a solvent may also be added to the system. Preferred solvents include toluene, xylene and 20 methylene chloride.

The present invention further provides a process for the polymerization or copolymerization of olefins and producing a polymer having a broad molecular weight distribution. The process comprises polymerizing a monoolefin, particularly propylene, or copolymerizing two or more olefins in the presence of a catalyst system as described. Again, it is possible to tailor the molecular weight distribution of a polymer by 25 selecting the appropriate combination of metallocene catalysts. The invention further provides a polyolefin with a relatively broad molecular weight distribution that is made by this process.

BRIEF DESCRIPTION OF THE FIGURES

30 The foregoing and additional objects and advantages of the invention will be more apparent when the following detailed description is read in conjunction with the accompanying Figures.

FIGURE 1 is a plot of the molecular weight distribution ("MWD") as derived from a GPC elution curve for the polypropylene produced in comparative Example A. It shows the high and narrow MWD obtained from using $Et(Ind)_2HfCl_2$ in a single catalyst system.

35 FIGURE 2 is a plot of the MWD of the polypropylene produced in comparative Example D showing the narrow MWD obtained from using $Et(IndH_4)_2ZrCl_2$.

FIGURE 3 is a plot of the MWD of the polypropylene produced in Example 1 in accordance with the present invention. In Example 1, propylene was polymerized using a catalyst system comprising two metallocene catalysts: $Et(Ind)_2HfCl_2$ and $Et(IndH_4)_2ZrCl_2$. FIGURE 3 shows the high and broad MWD 40 obtained by practicing the present invention. FIGURE 4 is a plot of the MWD for the polymer product of Example 2.

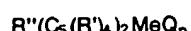
FIGURE 5 is a plot of the MWD for the polypropylene produced in Example 4.

FIGURE 6 is a plot of the MWD for the polypropylene produced in Example 7. This plot shows a broad distribution at a lower molecular weight than the other figures.

45 DETAILED DESCRIPTION

The present invention provides catalyst systems for use in the polymerization of olefins to obtain a polymer with a broad or multimodal molecular weight distribution (MWD). The invention is particularly 50 applicable to the polymerization of propylene because of the stereochemical control that the catalyst systems exhibit on the polymer and the systems ability to produce a polymer with a high isotactic index. The catalyst systems of the present invention, however, may be used to polymerize higher olefins as well as ethylene and copolymers of propylene and ethylene.

The catalyst systems of the present invention comprise at least two different metallocene catalysts 55 which are chiral and stereo-rigid in combination with an aluminum compound. The metallocene catalysts may be described by the formula:



wherein $(C_5(R')_4)$ is a cyclopentadienyl or substituted cyclopentadienyl ring; R' is a hydrogen or a hydrocarbyl radical having 1-20 carbon atoms, and each R' may be the same or each may be different; R'' connects the two $(C_5(R')_4)$ rings such that at least a portion of R'' acts as a bridge between the two rings and makes the catalyst stereo-rigid; Me is a Group 4b, 5b, or 6b metal of the Periodic Table; Q is a halogen or is a hydrocarbyl radical having 1-20 carbon atoms; and $0 \leq p \leq 3$.

R' may be hydrogen or a hydrocarbyl radical. Examples of hydrocarbyl radicals useful as R' include alkyl, alkenyl, aryl, alkylaryl or arylalkyl radicals. More specifically, exemplary hydrocarbyl radicals include methyl, ethyl, propyl, butyl, amyl, isoamyl, hexyl, isobutyl, heptyl, octyl, nonyl, decyl, cetyl, phenyl, methylene, ethylene, propylene, and other like groups. In a preferred embodiment, the R' 's are selected so that $(C_5(R')_4)$ is an indenyl radical (Ind) or a hydrated indenyl radical ($IndH_4$).

R'' is a stable component that bridges the two $(C_5(R')_4)$ rings in order to render the catalyst stereo-rigid. R'' may be organic or inorganic and may include groups depending from the portion acting as the bridge. Examples of R'' include an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl group, a germanium hydrocarbyl group, boron, nitrogen, sulfur, phosphorous, aluminum or groups containing boron, nitrogen, sulfur, phosphorous or aluminum, specifically an alkyl phosphine and an alkyl amine. The preferred R'' components are methylene ($-CH_2-$), ethylene ($-C_2H_4-$), an alkyl silicon, and a cycloalkyl silicon such as cyclopropyl silicon, among others.

Similarly, Q may be any of the hydrocarbyl groups listed for R' above, but preferably, Q is a halogen, and most preferably, Q is chlorine. Also in the preferred embodiment, p is 2.

The metallocene catalyst should be chiral, i.e., non-superimposable on its mirror image, for the polymerization of propylene and higher alpha-olefins in order to produce a useful polymer product. It was discovered that chirality in a metallocene catalyst exhibits stereochemical control over the polymer product and produces a polymer with a high isotactic index. In addition, the catalyst should be stereo-rigid to aid in the stereochemical control of the polymerization. It is not necessary for the catalyst to be chiral or stereo-rigid for the polymerization of ethylene or predominantly ethylene copolymers.

The present invention comprises the use of at least two different metallocene catalysts. The catalysts may differ in any one or more of the constituent groups : R'' , R'_m , Me , or Q_p . The appropriate groups may be varied and the catalyst system tailored to produce a polymer product with the desired MWD.

As shown in the Examples below, the combination of some catalysts produces a high and broad MWD, while other combinations produce a lower MWD. Varying the Me groups between hafnium, zirconium and titanium produces a particularly broad MWD.

The catalyst systems of the present invention also include an aluminum compound in combination with the metallocene catalysts. The aluminum compound may be alumoxane, trimethyl aluminum or mixtures thereof. Preferably, the aluminum compound is an alumoxane represented by the general formula $(R-Al-O)$ for the cyclic form and $R(R-Al-O)_n-AlR_2$ for the linear form. R is an alkyl group with preferably 1-5 carbons and n is an integer preferably from 1 to about 20. Most preferably, R is a methyl group. In a preferred embodiment, the aluminum compound may be a mixture of the linear and cyclic alumoxanes.

Generally, in preparing alumoxanes a mixture of the cyclic and linear forms is obtained.

The alumoxanes may be prepared using any of the methods known in the art. Preferably, they are prepared by contacting water with a solution of trialkyl aluminum, such as, for example, trimethyl aluminum in a suitable solvent such as benzene. Most preferably, the alumoxane is prepared in the presence of a hydrated copper sulfate as described in U.S. Patent No. 4,404,344, the disclosure of which is hereby incorporated by reference. As an example, this method of preparation comprises treating a dilute solution of trimethyl aluminum in toluene with copper sulfate represented by the formula $CuSO_4 \cdot 5H_2O$.

The aluminum compound of the present invention may also comprise a mixture of trimethyl aluminum (TMA) and alumoxane. As described in copending application Serial No. 034,341 filed on April 3, 1987, the addition of TMA with alumoxanes to the catalyst system causes a transformation of the catalyst over time with the transformed catalyst producing a product with different characteristics than the product of the initial catalyst system. Preferably, TMA is added in the amount of about 0-20 mole percent of the aluminum compound.

The catalyst system may also include a solvent to increase the solubility of the catalyst in the monomer. In a preferred embodiment, the olefin monomer is used in a liquid form. The solvent may be premixed with the catalyst or added with the monomer. The preferred solvents include toluene, xylene, and methylene chloride as well as other known solvents. Depending on the catalysts, a particular solvent may be more compatible with a particular catalyst than other solvents.

The metallocene catalysts useful in the present invention may be prepared by any of the methods known in the art. Typically, the procedures comprise the addition of a MeQ group and a R'' group to a starting

compound such as indene or another dicyclopentadiene compound. An example of a preferred preparation method is given below.

The catalyst system of the present invention may be used with any polymerization process. An example of a preferred procedure is described in co-pending application Serial No. 009,712, the disclosure of which is hereby incorporated by reference. This process includes a pre-polymerization of the catalyst before introducing the catalyst into a polymerization reaction zone. Another preferred procedure is described in the examples below.

The following Examples illustrate the present invention and its various advantages in more detail. Included as Examples A-D are comparative examples using only one metallocene catalyst in the system. Examples 1-7 illustrate the present invention by using catalyst systems with at least two different metallocene catalysts. The results are shown in Table 1 and Figures 1-6.

Example A

15 Preparation of a Metallocene Catalyst

A hafnium metallocene of the formula $\text{Et}(\text{Ind})_2\text{-HfCl}_2$ was prepared by first preparing the ligand $\text{Et}(\text{Ind})_2$. The ligand was prepared by adding 215 mmol of n-butyl lithium to 215 mmol of Gold Label indene (Aldrich) in 250 ml of dry, deoxygenated tetrahydrofuran (THF) under nitrogen at -91 °C. The reaction flask was warmed to 25 °C and stirred for 4 hours before 107 mmol of 1,2-C₂H₄Br₂ dissolved in 100 ml of THF were added to the indene anion under nitrogen at -91 °C. The mixture was stirred at 50 °C for 12 hours. Then, 20 ml of water were added dropwise and the ether evaporated to yield 16.4 grams (60%) of pale yellow solids.

Twenty-four cc of 1.6 M n-butyl lithium were added to 5 grams of $\text{Et}(\text{Ind})_2$ in 150 cc of tetrahydrofuran (THF) under a nitrogen atmosphere and at liquid nitrogen/heptane slush bath temperatures. The solution became orange-red after being held at 50 °C overnight. Thereafter, 6.21 grams (19.4 mmol) of HfCl₄ and 250 cc of THF were cooled separately under nitrogen in liquid nitrogen/heptane slush baths. The THF was added dropwise to the HfCl₄ and the solution gradually warmed to 50 °C to form a transparent, colorless solution. The warm THF solution of $\text{Et}(\text{Ind})_2\text{Li}_2$ was added by cannulation to the HfCl₄/THF solution at 50 °C; whereupon it became, sequentially, yellow and then orange-red. The mixture was held overnight at 50 °C. Sparging the reaction mixture for a few seconds with gaseous HCl resulted in a bright yellow solution. The solvent was removed under vacuum and the remaining yellow, viscous mass was vacuum dried to an orange cake overnight. The cake was pulverized and covered briefly with 80 cc of CH₂Cl₂. Decantation of the dark brown solution containing the surface impurities left 8 grams (dry weight) of a bright yellow powder. The yellow powder was dissolved in 100 cc of CH₂Cl₂ and the insoluble white LiCl filtered off. On addition of 1000 cc of cold pentane to the CH₂Cl₂ solution, 2 grams (dry weight) of a bright yellow powder precipitated. The complex was filtered off, dried and further purified by fractional recrystallization from dry toluene at 0 °C. The complexes were stored under argon and were recrystallized less than 3 weeks prior to a polymerization test.

40 Polymerization of Propylene

In a 75 ml stainless steel sample cylinder filled with argon, a catalyst solution containing 3.4 mg of $\text{Et}(\text{Ind})_2\text{HfCl}_2$ and toluene was precontacted for 5 minutes with a 10 ml toluene solution of 560 mg of alumoxane. The contents of the sample cylinder were then charged to a 4 liter Zipperclave reactor containing one liter of propylene and about 1 liter of toluene with the reactor at 50 °C. The temperature was maintained at the reaction temperature of 50 °C and the contents of the reactor were agitated for one hour. The propylene was then vented and the contents of the reactor were washed with 50% methanol in dilute HCl solution and dried in vacuo.

50 Analysis of Polymer

The polymer product was then analyzed for the melting points and molecular weights. The melting points (T_m) shown in Table 1 were derived from DSC (Differential Scanning Calorimetry) data as known in the art. The melting points are not true equilibrium melting points but are DSC peak temperatures. True equilibrium melting points obtained over a period of several hours would be higher than the DSC peak melting points.

EP 0 310 734 B1

The molecular weights of the polymers were calculated using GPC (Gel Permeation Chromatography) analysis. The analysis was done on a Waters 150 C instrument with a column of Jordi gel. The solvent was trichlorobenzene and the operating temperature was 140 °C. The values for M_n , M_v , M_z , M_w and M_w/M_n are reported in Table 1.

5

Examples B-D

Procedures similar to Example A were followed in preparing three different metallocene catalysts: Et IndH₄)₂HfCl₂ (Example B); Et Ind)₂ZrCl₂ (Example C); and Et(IndH₄)₂ZrCl₂ (Example D). Propylene was 10 polymerized as in Example A using each of these individual catalysts under the varying conditions as given in Table 1. Table 1 also shows the MWD obtained with these individual catalysts. In particular, the M_w/M_n values obtained with the single catalyst systems are all between 2.0-2.5, indicating a narrow MWD. Figures 1 and 2 show a plot of the GPC elution curves for Examples A and D respectively. Figure 1 shows a high, narrow MWD while Figure 2 exhibits a lower MWD.

15

Example 1

Two metallocene catalysts prepared as in Examples A and D were used together in the polymerization of propylene. The catalysts, Et(Ind)₂HfCl₂ and Et(IndH₄)₂ZrCl₂, were used in the amounts reflected in Table 20 1 and were precontacted with 700 mg of alumoxane in toluene as in Example A. The reaction temperature was 45 °C.

The polymer product exhibited a very broad MWD with $M_w/M_n = 9.9$. The plot of the MWD is shown in Figure 3. The use of the two metallocene catalysts as taught by the present invention caused a dramatic change in the MWD as compared to either of the single catalyst systems as shown in Figures 1 or 2.

25

Examples 2-7

Similar to Example 1, Examples 2-7 used two different metallocene catalysts as indicated in Table 1 and under the polymerization conditions shown in Table 1. The MWD for Examples 2, 4, and 7 are plotted 30 in Figures 4, 5, and 6 respectively. These results show an ability to vary the breadth and the values of the MWD by using different combinations of various metallocene catalysts as described by the present invention.

The Examples illustrate the present invention with Hf and Zr metallocene catalysts. Other transition metals are also useful in the present invention. The amounts of the catalysts may be varied to achieve 35 different MWD. Similarly, different polymerization procedures may be used as well as different conditions, such as temperature and the addition of a solvent, to achieve different results.

40

45

50

55

TABLE I

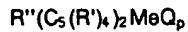
x:	<u>Hf Catalyst</u>	<u>Zr Catalyst</u>	<u>Hf</u> mg	<u>η_r</u> mg	<u>Alumoxane</u>	<u>Toluene</u> 1 °C	<u>Yield</u> g	<u>M_n</u> /1000 °C	<u>M_w</u> /1000 °C	<u>M_w</u> /M _n
Et(Ind) ₂ HfCl ₂	3.4	560	1.0	50	230.0	134	130	277	304	5.38
Et(IndI ₄) ₂ HfCl ₂	1.72	280	0.5	50	127.1	143	74	142	155	2.1
Et(Ind) ₂ ZrCl ₂	1.46	280	0.5	40	201.0	137	16	29	31	4.8
Et(IndI ₄) ₂ ZrCl ₂	1.45	280	0.5	50	31.0	138	7.5	17	19	4.4
Et(Ind) ₂ HfCl ₂	1.04	700	1.0	45	12.5	137	25	204	244	5.84
Et(Ind) ₂ HfCl ₂	1.05	0.04	280	1.0	45	5.5	138	16	132	16.9
Et(Ind) ₂ HfCl ₂	1.03	0.21	280	0	45	15.0	136	11	73	10.3
Et(Ind) ₂ HfCl ₂	1.2	0.2	380	0	80	47.0	128	16	70	80
Et(Ind) ₂ HfCl ₂	1.0	0.3	380	0	80	56.0	126	12	42	4.9
Et(Ind) ₂ HfCl ₂	1.0	0.4	380	0	80	75.0	125	8.4	27	3.2
Et(IndI ₄) ₂ HfCl ₂	1.0	0.4	380	0	80	175.0	125	8.0	26	3.0
Et(IndI ₄) ₂ ZrCl ₂	1.0	0.4	380	0	80	175.0	125	8.0	26	3.7

Claims

55

1. A catalyst system for the polymerization and copolymerization of olefins having 3-8 carbon atoms, said system comprising :

a) at least two different metallocene catalysts which are chiral and stereo-rigid and are described by the formula :



5 wherein $(C_5(R')_4)$ is a cyclopentadienyl or substituted cyclopentadienyl ring; each R' is the same or different and is a hydrogen or a hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the two $(C_5(R')_4)$ rings imparting stereo-rigidity to said catalysts, and R'' is selected from the group consisting of an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, boron, nitrogen, sulfur, phosphorous, aluminum and groups containing boron, nitrogen, sulfur, phosphorous or aluminum ; Me is a group 4b, 5b or 6b metal as designated in the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; 0 ≤ p ≤ 3; and in at least one of said metallocene catalyst Me is hafnium; and (b) an aluminum compound selected from the group consisting of alumoxane, trimethyl aluminum, and mixtures thereof.

2. The catalyst system of Claim 1 wherein Me is selected from hafnium, zirconium and titanium.
 3. The catalyst system of Claim 1 wherein the system contains at least one zirconocene catalyst.
 4. The catalyst system of Claim 1 wherein $(C_5(R')_4)$ is selected from the group consisting of an indenyl radical and a hydrated indenyl radical.
 5. The catalyst system of Claim 1 wherein R'' is an ethylene radical for at least one of the catalysts.
 6. The catalyst system of Claim 1 further comprising :
 - c) a solvent that increases the solubility of the catalyst in an olefin monomer.
 7. The catalyst system of Claim 1, wherein R'' is selected from the group consisting of an alkyl phosphine and an alkyl amine.
 8. A process for the polymerization and copolymerization of olefins having 3-8 carbon atoms comprising :
 - (1) providing a catalyst system comprising :
 - a) at least two different metallocene catalysts which are chiral and stereo-rigid and are described by the formula :
- 35
- 40
- 45
- 50
- 55
8. A process for the polymerization and copolymerization of olefins having 3-8 carbon atoms comprising :
 - (1) providing a catalyst system comprising :
 - a) at least two different metallocene catalysts which are chiral and stereo-rigid and are described by the formula :
- R''(C₅(R')₄)₂MeQ_p
- wherein $(C_5(R')_4)$ is a cyclopentadienyl or substituted cyclopentadienyl ring; each R' is the same or different and is a hydrogen or a hydrocarbyl radical having 1-20 carbon atoms; R'' is a structural bridge between the two $(C_5(R')_4)$ rings imparting stereo-rigidity to said catalysts, and R'' is selected from the group consisting of an alkylene radical having 1-4 carbon atoms, a silicon hydrocarbyl radical, a germanium hydrocarbyl radical, boron, nitrogen, sulfur, phosphorous, aluminum and groups containing boron, nitrogen, sulfur, phosphorous or aluminum, Me is a group 4b, 5b or 6b metal as designated in the Periodic Table of Elements; each Q is a hydrocarbyl radical having 1-20 carbon atoms or is a halogen; 0 ≤ p ≤ 3; and in at least one of said metallocene catalyst Me is hafnium; and (b) an aluminum compound selected from the group consisting of alumoxane, trimethyl aluminum, and mixtures thereof.
- (2) contacting said catalyst system with an olefin monomer under polymerization conditions suitable for producing polyolefins.
9. The process of Claim 8 wherein Me is selected from hafnium, zirconium and titanium.
10. The process of Claim 8 wherein the catalyst system further comprises : (c) a solvent that increases the solubility of the catalyst in an olefin monomer.

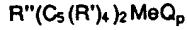
11. The process of Claim 8 wherein the olefin monomer is propylene or a mixture of propylene and another olefin monomer.

5 12. The process of Claim 8 wherein R" is selected from the group consisting of an alkyl phosphine and an alkyl amine.

Patentansprüche

1. Katalysatorsystem zur Polymerisation und Copolymerisation von Olefinen, die 3 - 8 Kohlenstoff-Atome 10 aufweisen, wobei besagtes Katalysatorsystem umfaßt:

- a) mindestens zwei verschiedene Metallocenkatalysatoren, die chiral und stereorigid sind und durch die Formel beschrieben werden:



15 worin $(C_5(R')_4)$ ein Cyclopentadienyl- oder ein substituierter Cyclopentadienylring ist; jedes R' gleich oder verschieden ist und ein Wasserstoff- oder ein Kohlenwasserstoffradikal mit 1 - 20 Kohlenstoff-Atomen ist; R'' eine strukturelle Brücke zwischen den beiden $(C_5(R')_4)$ -Ringern ist, die den besagten Katalysatoren Stereorigidität verleiht, und R'' aus der Gruppe ausgewählt ist, die aus einem Alkylenradikal mit 1 - 4 Kohlenstoffatomen, einem Silicium-Kohlenwasserstoffradikal, einem Germanium-Kohlenwasserstoffradikal, Bor, Stickstoff, Schwefel, Phosphor, Aluminium und Gruppen, die Bor, 20 Stickstoff, Schwefel, Phosphor oder Aluminium enthalten, besteht; Me ein Metall der im Periodensystem der Elemente aufgezeigten Gruppe 4b, 5b oder 6b ist; jedes Q ein Kohlenwasserstoffradikal mit 1-20 Kohlenstoffatomen ist oder ein Halogen ist; 0 ≤ p ≤ 3; und in mindestens einem der besagten Metallocenkatalysatoren Me Hafnium ist; und

25 b) eine Aluminiumverbindung, die aus der Gruppe ausgewählt ist, die aus Alumoxan, Trimethylaluminium und deren Mischungen besteht.

2. Katalysatorsystem nach Anspruch 1, worin Me aus Hafnium, Zirkonium und Titan ausgewählt ist.

30 3. Katalysatorsystem nach Anspruch 1, worin das System mindestens einen Zirkonocenkatalysator enthält.

4. Katalysatorsystem nach Anspruch 1, worin $(C_5(R')_4)$ aus der Gruppe ausgewählt ist, die aus einem Indenylradikal und einem hydrierten Indenylradikal besteht.

35 5. Katalysatorsystem nach Anspruch 1, worin R'' bei wenigstens einem der Katalysatoren ein Ethylenradikal ist.

6. Katalysatorsystem nach Anspruch 1, welches weiterhin umfaßt:

40 c) ein Lösungsmittel, das die Löslichkeit des Katalysators in einem Olefinmonomer erhöht.

7. Katalysatorsystem nach Anspruch 1, worin R'' aus der Gruppe ausgewählt ist, die aus einem Alkylphosphan und einem Alkylamin besteht.

45 8. Verfahren zur Polymerisation und Copolymerisation von Olefinen mit 3 - 8 Kohlenstoffatomen, welches umfaßt:

(1) Bereitstellung eines Katalysatorsystems, das umfaßt:

- a) mindestens zwei verschiedene Metallocenkatalysatoren, die chiral und stereorigid sind, und die durch die Formel beschrieben werden:

50 R'' $(C_5(R')_4)_2MeQ_p$

worin $(C_5(R')_4)$ ein Cyclopentadienyl- oder substituierter Cyclopentadienylring ist; jedes R' gleich oder verschieden ist und ein Wasserstoff- oder ein Kohlenwasserstoffradikal mit 1 - 20 Kohlenstoffatomen ist; R'' eine strukturelle Brücke zwischen den beiden $(C_5(R')_4)$ -Ringern ist, die den besagten Katalysatoren Stereorigidität verleiht, und R'' aus der Gruppe ausgewählt ist, die aus einem Alkylenradikal mit 1 - 4 Kohlenstoffatomen, einem Silicium-Kohlenwasserstoffradikal, einem Germanium-Kohlenwasserstoffradikal, Bor, Stickstoff, Schwefel, Phosphor, Aluminium und Gruppen, die Bor, 55 Stickstoff, Schwefel, Phosphor oder Aluminium enthalten, besteht; Me ein Metall der im Periodensystem der Elemente aufgezeigten Gruppe 4b, 5b oder 6b ist; jedes Q ein Kohlenwasserstoffradikal mit 1-20 Kohlenstoffatomen ist oder ein Halogen ist; 0 ≤ p ≤ 3; und in mindestens einem der besagten Metallocenkatalysatoren Me Hafnium ist; und

pen, die Bor, Stickstoff, Schwefel, Phosphor oder Aluminium enthalten, besteht; Me ein im Periodensystem der Elemente aufgezeigtes Metall der Gruppe 4b, 5b oder 6b ist; jedes Q ein Kohlenwasserstoffradikal mit 1 - 20 Kohlenstoffatomen ist oder ein Halogen ist; 0 ≤ p ≤ 3; und in mindestens einem der besagten Metallocenkatalysatoren Me Hafnium ist; und

5 (b) eine Aluminiumverbindung, die aus der Gruppe ausgewählt wird, die aus Alumoxan, Trimethylaluminium und deren Mischungen besteht.

(2) Zusammenbringen des Katalysatorsystems mit einem Olefinmonomer unter Polymerisationsbedingungen, die zur Herstellung von Polyolefinen geeignet sind.

10 9. Verfahren nach Anspruch 8, worin Me aus Hafnium, Zirkonium und Titan ausgewählt wird.

10. Verfahren nach Anspruch 8, worin das Katalysatorsystem weiterhin umfaßt:

(c) ein Lösungsmittel, das die Löslichkeit des Katalysators in einem Olefinmonomer erhöht.

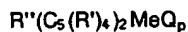
15 11. Verfahren nach Anspruch 8, worin das Olefinmonomer Propylen oder eine Mischung von Propylen und einem anderen Olefinmonomer ist.

12. Verfahren nach Anspruch 8, worin R" aus der Gruppe ausgewählt wird, die aus einem Alkylphosphan und einem Alkyamin besteht.

20 Revendications

1. Système catalytique pour la polymérisation et la copolymérisation d'oléfines possédant 3 à 8 atomes de carbone, le dit système comprenant :

25 a) au moins deux catalyseurs métallocènes différents qui sont chiraux et stéréorigides et sont décrits par la formule :



30 dans laquelle $(C_5(R')_4)$ est un cyclopentadiényl ou un anneau cyclopentadiényl substitué; chaque R' est identique ou différent et est un hydrogène ou un radical hydrocarbyl possédant 1 à 20 atomes de carbone; R" est un pont structurel entre deux anneaux $(C_5(R')_4)$ procurant la stéréorigidité aux dits catalyseurs, et R" est choisi parmi les éléments du groupe constitué d'un radical alkylène comprenant 1 à 4 atomes de carbone, un radical hydrocarbyl silicone, un radical hydrocarbyl germanium, le bore, l'azote, le soufre, le phosphore, l'aluminium, et des groupes contenant du bore, de l'azote, du soufre, du phosphore ou de l'aluminium; Me est un métal des groupes 4b, 5b ou 6b tels que désignés dans le Tableau Périodique des Eléments; chaque Q est un radical hydrocarbyl possédant 1 à 20 atomes de carbone ou est un halogène; 0 ≤ p ≤ 3; et Me est l'hafnium dans au moins un des dits catalyseurs métallocènes; et

40 b) un composé aluminium choisi parmi les éléments du groupe constitué d'alumoxane, de triméthylaluminium, et des mélanges de ceux-ci.

2. Le système catalytique de la revendication 1 dans lequel Me est choisi parmi l'hafnium, le zirconium et le titane.

45 3. Le système catalytique de la revendication 1 dans lequel le système contient au moins un catalyseur zirconocène.

4. Le système catalytique de la revendication 1 dans lequel $(C_5(R')_4)$ est choisi parmi les éléments du groupe constitué d'un radical indényle et d'un radical indényle hydraté.

5. Le système catalytique de la revendication 1 dans lequel R" est un radical éthylène pour au moins un des catalyseurs.

55 6. Le système catalytique de la revendication 1 comprenant en plus :
c) un solvant qui accroît la solubilité du catalyseur dans une oléfine monomère.

7. Le système catalytique de la revendication 1 dans lequel R" est choisi parmi les éléments du groupe constitué d'une alkyl phosphine et d'une alkyl amine.

5 8. Procédé de polymérisation et de copolymérisation d'oléfines ayant de 3 à 8 atomes de carbone comprenant:

(1) la fourniture d'un système catalytique comprenant:

a) au moins deux catalyseurs métallocènes différents qui sont chiraux et stéréorigides et qui sont décrits par la formule:

10 $R''(C_5(R')_4)_2MeQ_p$

15 dans laquelle $(C_5(R')_4)$ est un cyclopentadiényle ou un anneau cyclopentadiényle substitué; chaque R' est identique ou différent et est un hydrogène ou un radical hydrocarbyl possédant 1 à 20 atomes de carbone; R" est un pont structurel entre deux anneaux $(C_5(R')_4)$ procurant la stéréorigidité aux dits catalyseurs, et R" est choisi parmi les éléments du groupe constitué d'un radical alkylène comprenant 1 à 4 atomes de carbone, un radical hydrocarbyl silicone, un radical hydrocarbyl germanium, le bore, l'azote, le soufre, le phosphore, l'aluminium, et des groupes contenant du bore, de l'azote, du soufre, du phosphore ou de l'aluminium; Me est un métal des groupes 4b, 5b ou 6b tels que désignés dans le Tableau Périodique des Éléments; chaque Q est un radical hydrocarbyl possédant 1 à 20 atomes de carbone ou est un halogène; 0 ≤ p ≤ 3; et Me est l'hafnium dans au moins un des dits catalyseurs métallocènes; et

20 b) un composé aluminium choisi parmi les éléments du groupe constitué d'alumoxane, de triméthyl aluminium, et des mélanges de ceux-ci.

25 (2) la mise en contact du dit catalyseur avec une oléfine monomère dans des conditions de polymérisation appropriées pour la production de polyoléfines.

9. Le procédé de la revendication 8 dans lequel Me est choisi parmi l'hafnium, le zirconium et le titane.

10. Le procédé de la revendication 8 dans lequel le système catalytique comprend en plus :

30 c) un solvant qui accroît la solubilité du catalyseur dans une oléfine monomère.

11. Le procédé de la revendication 8 dans lequel l'oléfine monomère est le propylène ou un mélange de propylène et d'une autre autre oléfine monomère.

35 12. Le procédé de la revendication 8 dans lequel R" est choisi parmi les éléments du groupe constitué d'une alkyl phosphine et d'une alkyl amine.

40

45

50

55

EP 0 310 734 B1

FIGURE 1

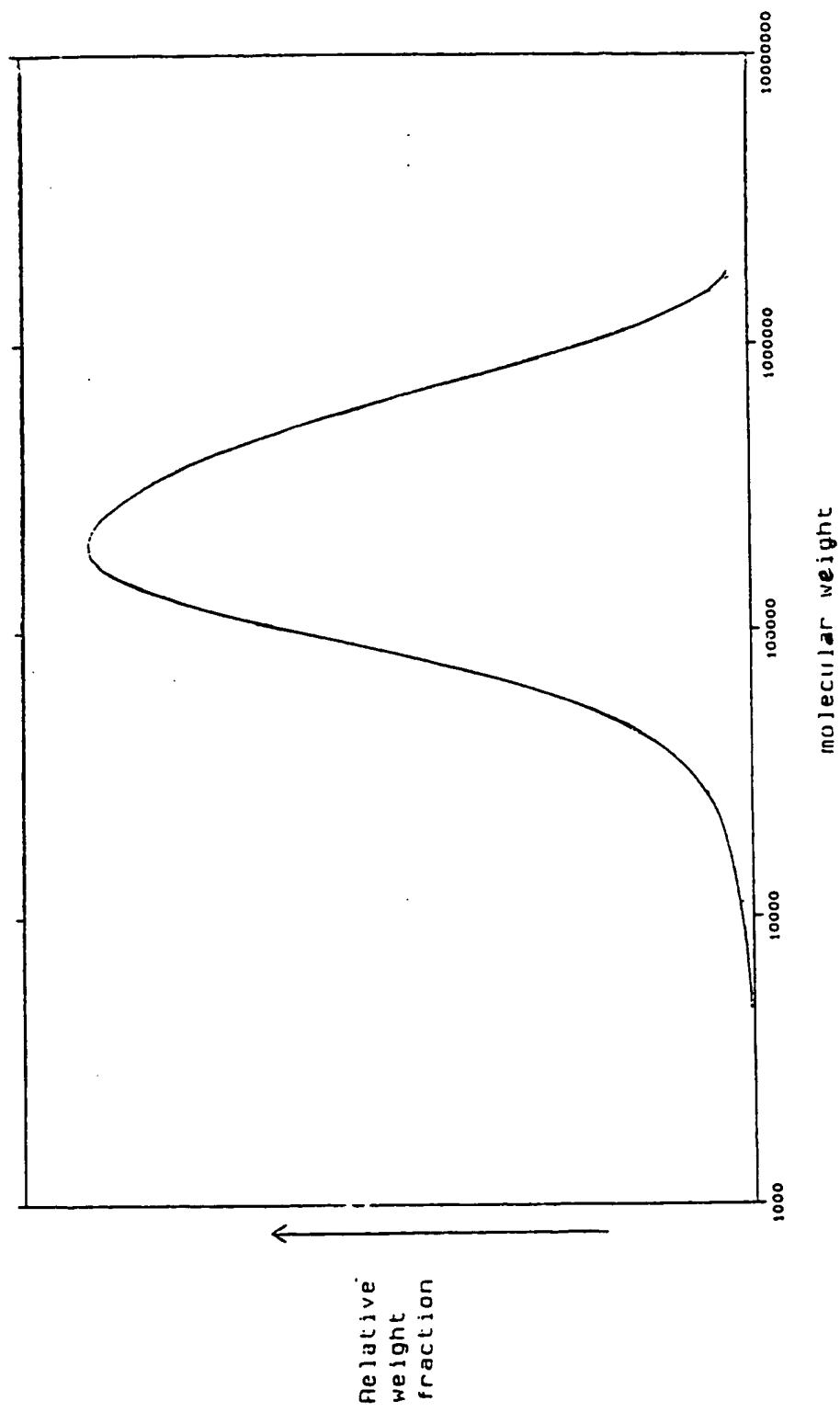


FIGURE 2

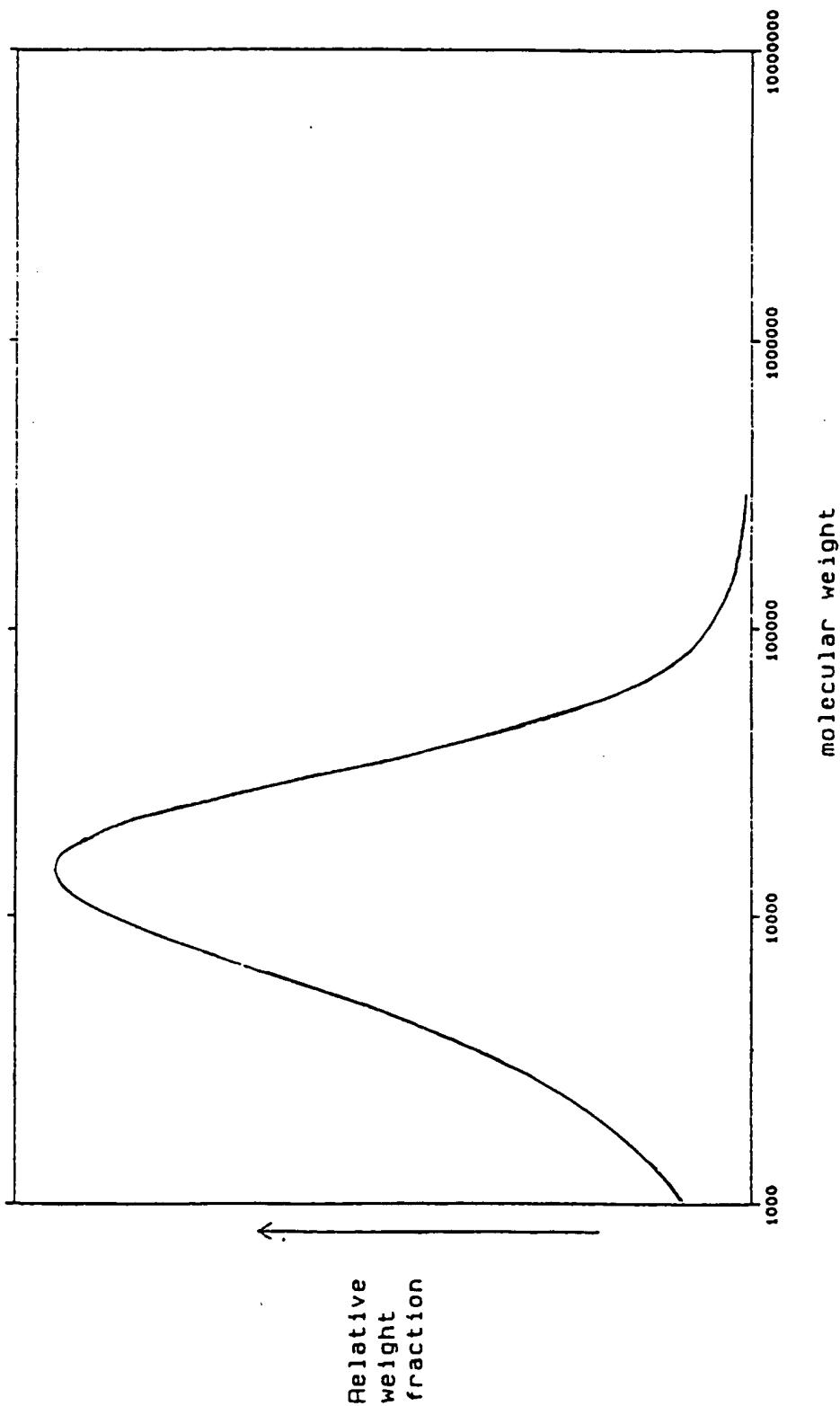


FIGURE 3

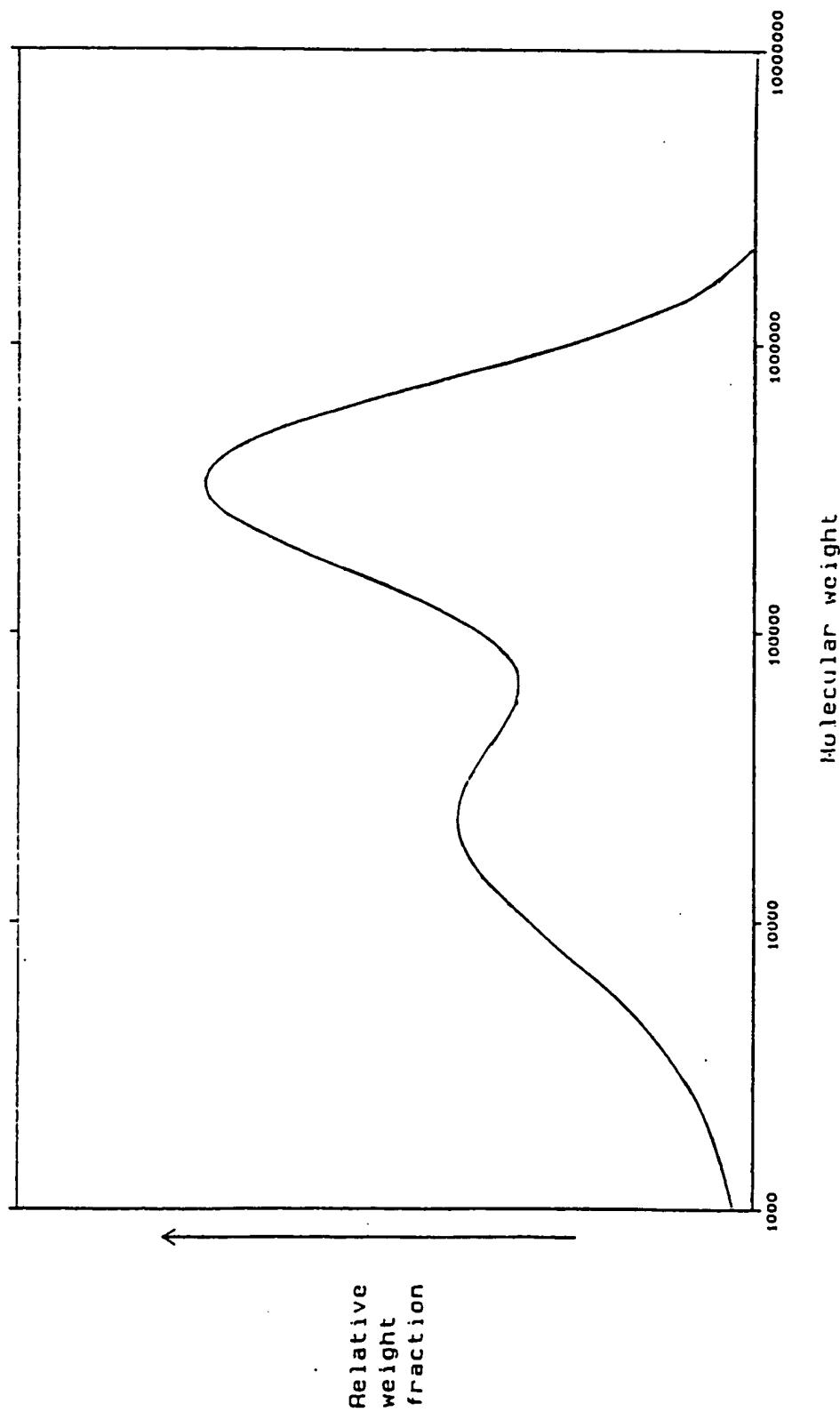


FIGURE 4

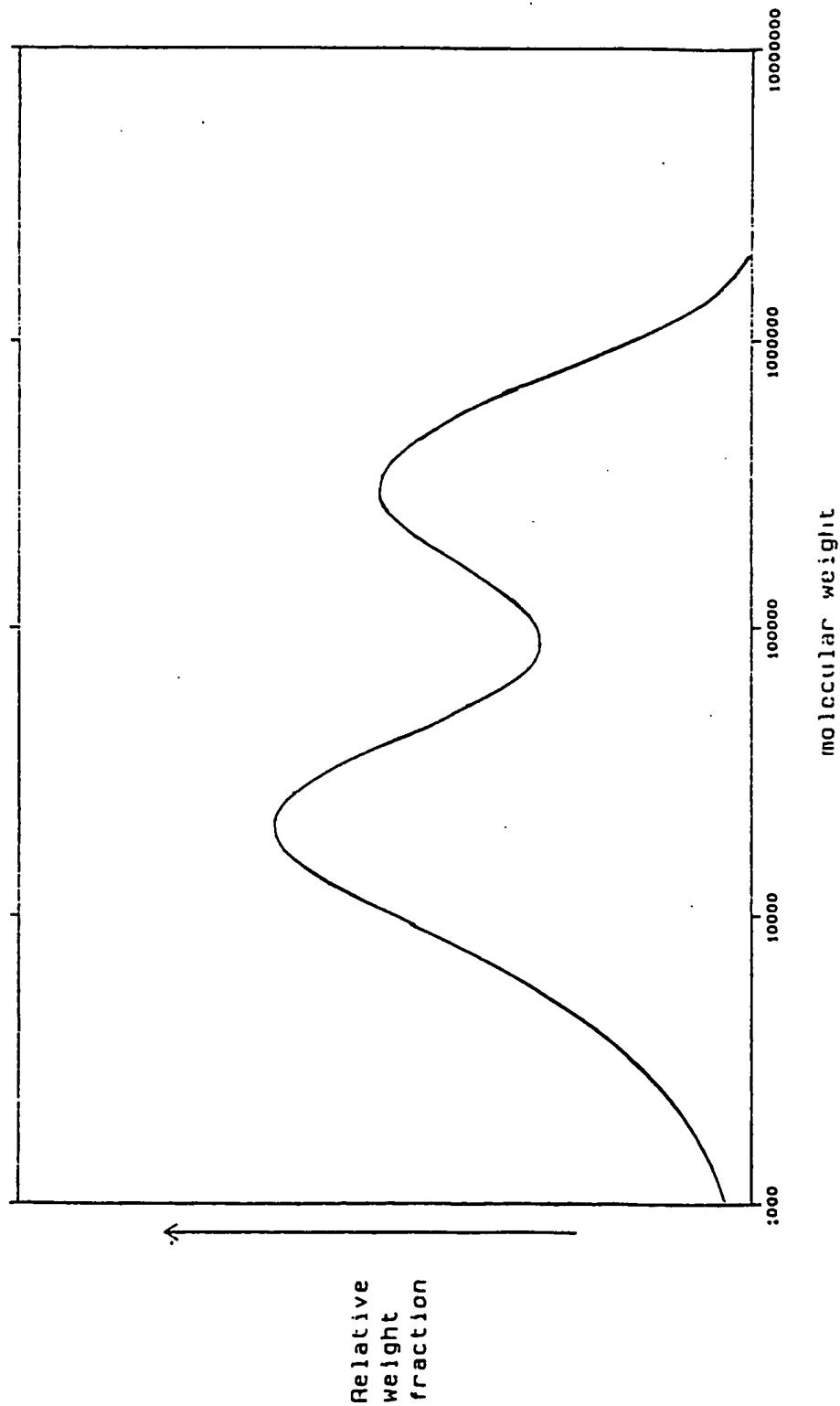


FIGURE 5

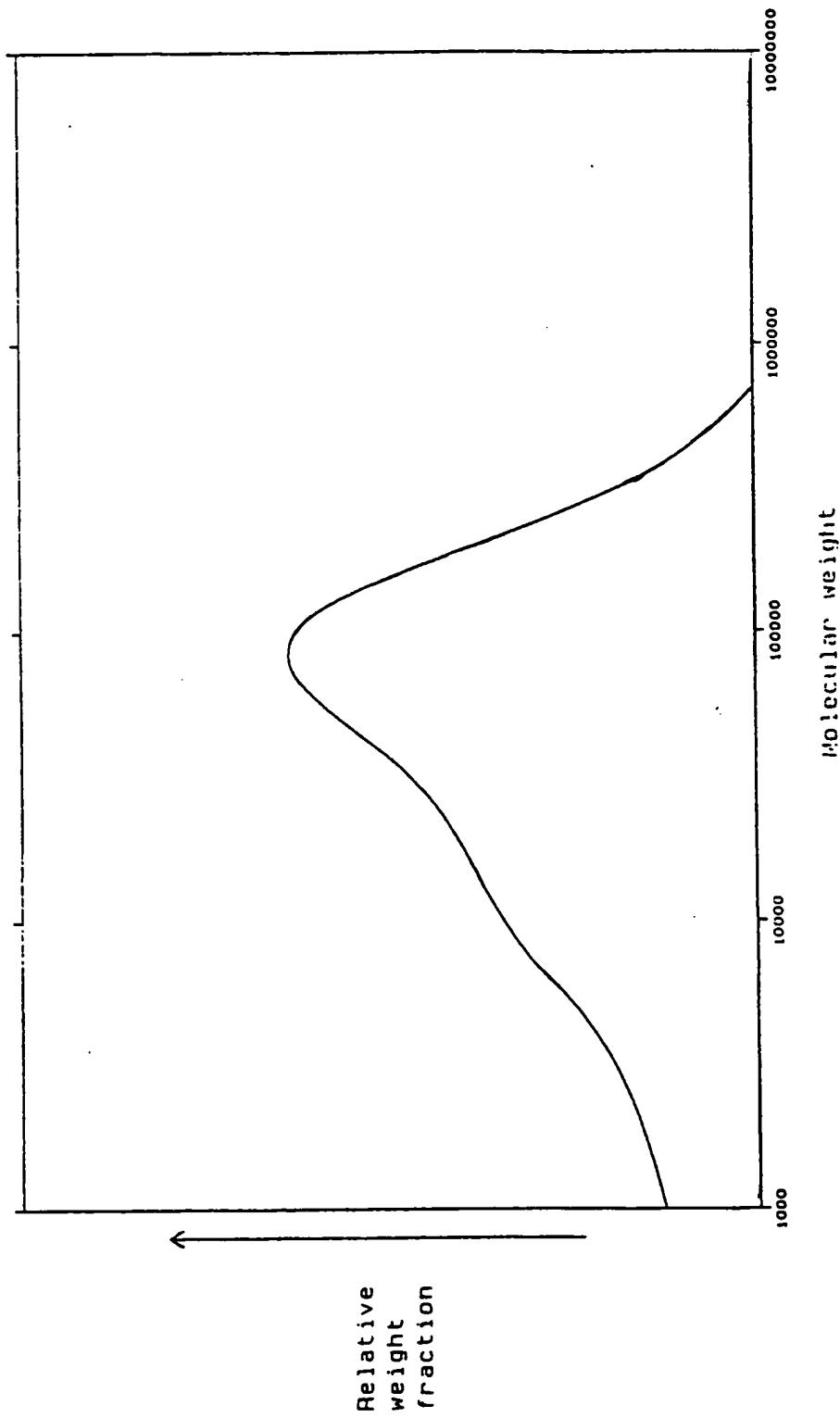


FIGURE 6

